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Molecular Orientational Distribution at Interfaces Using Second Harmonic Generation

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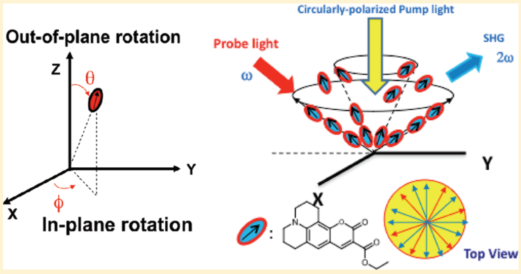
ABSTRACT: We present a novel method for obtaining the orientational distribution of molecules at the air/water interface by using a circularly polarized pump pulse that is incident normal to the interface to excite interfacial molecules to their excited electronic states. The second harmonic generation intensities of two linearly polarization combinations (45°-in/S-out and P-in/P-out) were measured. The ratio of their intensities measured before and after the pump pulse was then used to obtain the mean orientational angle and the orientational distribution utilizing a Gaussian distribution. The mean orientational angle and the orientational distribution of the organic dye molecule, coumarin 314, at the air/water interface were found to be 55 ± 2° with respect to the surface normal and a full width at half-maximum of 16 ± 3°.



INTRODUCTION

Understanding molecular orientation and its distribution at interfaces is of fundamental and practical importance.[1−3] One application where information on molecular orientation and distribution can be particularly important is in orientation-dependent intermolecular energy transfer and chemical and biomolecular reactions occurring at interfaces.[4−7] The likelihood of this occurring and, thus, the fraction of energy that is transferred are related to the orientation factor for transfer between the reactants with mean orientational angles and their orientational distributions.[1,7−9] The geometric orientation and its distribution of adsorbates at interfaces determine their structural and reactivity in interfacial environments.[1,7−9]

The general approach to investigate ultrafast molecular rotation is to use a polarized pump pulse, which preferentially photoselects ground state molecules whose transition moments are aligned parallel to the pump electric field. This perturbation of the equilibrium ground state orientation decays as the ground state molecules return to their equilibrium orientational distribution. This dynamic reorientation has been monitored by time-delayed probe pulses. With respect to the excited state molecules, they reorient to their equilibrium orientational distribution, which can be followed by fluorescence and by other probe methods.[1,10] To investigate molecular rotation and any other ultrafast processes at interfaces, it has been shown that the interface-selective methods of second harmonic generation (SHG) and sum frequency generation (SFG) are of marked values.[11−29] However, as stated in the literature,[30] "...A significant problem in interfacial spectroscopy is the independent determination of both the mean angle of a molecular axis and the angular distribution...". One interesting approach to obtain the orientational distribution of interfacial molecules has been made by combining SHG measurements with linear dichroism measurements.[12,30−34] However, this method, although useful, is limited to systems, in which the molecules of interest are present only at the liquid interface, not in the bulk liquid, for example, a Langmuir monolayer.

More often than not, interfacial molecular orientation distribution is assumed to be very narrow with a δ-function distribution. In this way, a mean orientational angle is extracted from experimental data.[23,35−37] Although useful, knowledge of the mean orientation is not sufficient to assess macroscopic order at interfaces.[38−40] In fact, molecular orientation distribution at interfaces may not be narrow in many cases, especially at the air/water interface, in that thermal fluctuations and the resultant surface roughness broaden molecular orientational profiles.[12,31−33] Furthermore, photoexcitation of interfacial molecules with a polarized pump pulse perturbs the orientational distribution of the ground state molecules. If the interfacial molecules have a δ-function distribution, the pump pulse would only decrease the number of ground state molecules without changing the orientational distribution; that is, the remaining ground state molecules would have the same δ-function orientation as before the pump pulse. As a consequence, there would be no time-dependent recovery in the few hundred picosecond characteristic of orientational relaxation of the probe molecule.[38−40] Here, we present a novel approach for measuring the mean orientational angle and orientational distribution of interfacial molecules.

THEORY

The SHG intensity of any polarization combinations at equilibrium, $I_{2\omega}^{\Lambda\text{-in}/\Lambda'\text{-out}}$, can be formulated with a fundamental

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beam, I_ω, as the following generalized expression[35,41−43]

$$\begin{aligned} I_{2\omega}^{\Lambda\text{-in}/\Lambda'\text{-out}} &\propto |\chi^{(2)}_{\Lambda\text{-in}/\Lambda'\text{-out}}|^2 \\ &= |[\hat{e}_{\Lambda'}(2\omega)\cdot L(2\omega)]\cdot \chi^{(2)}_{IJK} : [\hat{e}_{\Lambda}(\omega)\cdot L(\omega)][\hat{e}_{\Lambda}(\omega)\cdot L(\omega)]|^2 \end{aligned} \tag{1}$$

where Λ and Λ' are input and output light polarization angles with respect to the incident plane. The $\chi^{(2)}_{IJK}$ is second order susceptibility of interfaces, which is related to molecular hyperpolarizability $\alpha^{(2)}_{ijk}$ by the following expression.[35,43]

$$\chi^{(2)}_{IJK} = N \sum_{ijk} \langle R_{Ii} R_{Jj} R_{Kk} \rangle \alpha^{(2)}_{ijk} \tag{2}$$

where R_{Ii}, R_{Jj}, and R_{Kk} are the direction cosine matrix that transforms the laboratory frame (I, J, K) into the molecular frame (i, j, k), N is the number of ground state molecules at the surface at equilibrium, and $\langle\ \rangle$ denotes the ensemble average of an orientational probability distribution. The orientational probability distribution of finding a ground state adsorbate with out-of-plane angle θ and in-plane angle ϕ is $\rho_g(\theta, \phi; t < 0)$.[40] Prior to photoexcitation, by symmetry, only the seven elements $\chi^{(2)}_{XZX} = \chi^{(2)}_{YZY}$, $\chi^{(2)}_{ZXX} = \chi^{(2)}_{ZYY}$, $\chi^{(2)}_{XXZ} = \chi^{(2)}_{YYZ}$, and $\chi^{(2)}_{ZZZ}$ are nonzero at liquid surface (the X and Y axes are equivalent for an isotropic surface).[43] The hyperpolarizability $\alpha^{(2)}$ can be assumed to be uniaxial with only one element $\alpha^{(2)}_{zzz}$ in the case when the SHG wavelength is strongly resonant with a transition along the molecular axis z. Thus, the first six $\chi^{(2)}_{IJK}$ are equal in both magnitude and sign. Because of isotropic properties in the liquid surface plane, the in-plane angle ϕ is integrated out, and consequently, the orientational distribution function of ground state molecules depends only on θ, that is, $\rho_g(\theta, t < 0)$. Thus, the seven nonvanishing susceptibilities at equilibrium, that is, before photoexcitation, are[35,43]

$$\begin{aligned} \chi^{(2)}_{g,ZZZ}(t<0) &= N_g(t<0)\langle \cos^3\theta\rangle_{\rho_g(\theta,t<0)}\,\alpha^{(2)}_{g,zzz} \\ &= N_g(t<0)\alpha^{(2)}_{g,zzz}\int d\theta \sin\theta \cos^3\theta\, \rho_g(\theta,t<0) \\ \chi^{(2)}_{g,XZX}(t<0) &= \chi^{(2)}_{g,YZY} = \chi^{(2)}_{g,ZXX} = \chi^{(2)}_{g,ZYY} = \chi^{(2)}_{g,XXZ} = \chi^{(2)}_{g,YYZ} \\ &= \frac{1}{2} N_g(t<0)(\langle\cos\theta\rangle_{\rho_g(\theta,t<0)} - \langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)})\alpha^{(2)}_{g,zzz} \\ &= \frac{1}{2} N_g(t<0)\alpha^{(2)}_{g,zzz}\int d\theta \sin\theta(\cos\theta - \cos^3\theta)\rho_g(\theta,t<0) \end{aligned} \tag{3}$$

According to eqs 1 and 3, we can readily express susceptibilities $\chi^{(2)}_{45°\text{-in/S-out}}$ and $\chi^{(2)}_{\text{P-in/P-out}}$ of the ground state of interfacial molecules as the following[22,35,43,44]

$$\begin{aligned} \chi^{(2)}_{g,45°\text{-in/S-out}}(t<0) = {} & L_{XX}(2\omega)L_{ZZ}(\omega)L_{XX}(\omega)\cos 45°\sin\gamma_{\text{in}} \\ & \sin 45°\,\chi^{(2)}_{g,XZX}(t<0) + L_{XX}(2\omega)L_{XX}(\omega)L_{ZZ}(\omega)\sin 45° \\ & \cos 45°\sin\gamma_{\text{in}}\,\chi^{(2)}_{g,XXZ}(t<0) \\ \chi^{(2)}_{g,\text{P-in/P-out}}(t<0) = {} & -L_{YY}(2\omega)L_{ZZ}(\omega)L_{YY}(\omega)\cos\gamma_{\text{out}} \\ & \sin\gamma_{\text{in}}\cos\gamma_{\text{in}}\,\chi^{(2)}_{g,YZY}(t<0) - L_{YY}(2\omega)L_{YY}(\omega)L_{ZZ}(\omega) \\ & \cos\gamma_{\text{out}}\cos\gamma_{\text{in}}\sin\gamma_{\text{in}}\,\chi^{(2)}_{g,YYZ}(t<0) + L_{ZZ}(2\omega)L_{YY}(\omega)L_{YY}(\omega) \\ & \sin\gamma_{\text{out}}\cos\gamma_{\text{in}}\cos\gamma_{\text{in}}\,\chi^{(2)}_{g,ZYY}(t<0) + L_{ZZ}(2\omega)L_{ZZ}(\omega)L_{ZZ}(\omega) \\ & \sin\gamma_{\text{out}}\sin\gamma_{\text{in}}\sin\gamma_{\text{in}}\,\chi^{(2)}_{g,ZZZ}(t<0) \end{aligned} \tag{4}$$

where $L_{II}(\omega^i)$ is a local field factor, which is readily calculated based on the literature.[35,42,43] The γ_{in} and γ_{out} are the angles of the incident light and of the outgoing SHG light with respect to the surface normal. It is very important to note that the 45°-in/S-out and P-in/P-out SHG intensities can be written in the following general formula[23,37,45−48]

$$\begin{aligned} I_{2\omega}^{\Lambda\text{-in}/\Lambda'\text{-out}}(t<0) \propto {} & |AN_g(t<0)\alpha^{(2)}_{g,zzz}(\langle\cos\theta\rangle_{\rho_g(\theta,t<0)} \\ & - c\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)})|^2 \end{aligned} \tag{5}$$

where the coefficients A and c are functions of the incident and outgoing angles with respect to the surface normal, and local field factors are related to the dielectric constants of both the fundamental and the second harmonic light frequencies in the two bulk media and in the molecular layer.[22,23] In our case, $A = 0.08$, $c = 1$ for the 45°-in/S-out experiment; and $A = -0.048$, $c = 4.56$ for the P-in/P-out experiment. Thus, the ratio of 45°-in/S-out SHG intensity to P-in/P-out SHG intensity is given by

$$\begin{aligned} & \frac{I_{2\omega}^{45°\text{-in/S-out}}(t<0)}{I_{2\omega}^{\text{P-in/P-out}}(t<0)} \\ & = \frac{\left|0.08\alpha^{(2)}_{g,zzz}(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle)\right|^2}{\left|(-0.048)\alpha^{(2)}_{g,zzz}(\langle\cos\theta\rangle - 4.56\langle\cos^3\theta\rangle)\right|^2} \\ & = \frac{\left|0.08\left(\dfrac{\langle\cos\theta\rangle}{\langle\cos^3\theta\rangle} - 1\right)\right|^2}{\left|-0.048\left(\dfrac{\langle\cos\theta\rangle}{\langle\cos^3\theta\rangle} - 4.56\right)\right|^2} \end{aligned} \tag{6}$$

We introduce an interfacial order parameter at equilibrium, that is, before photoexcitation, $R(t < 0)$,[22,31,32,35,43,44] which is given by

$$\frac{\langle\cos\theta\rangle}{\langle\cos^3\theta\rangle} = R(t<0) \tag{7}$$

Thus, the measurement of the intensity ratio together with eq 6 yields $R(t < 0)$.

Upon photoexcitation, the transient SHG intensity, for any polarization combination, is a coherent mixing of the ground state and excited state susceptibilities[38,40,49,50]

$$I_{\text{total},2\omega}^{\Lambda\text{-in}/\Lambda'\text{-out}}(t) \propto \left|\chi^{(2)}_{g,\Lambda\text{-in}/\Lambda'\text{-out}}(t) + \chi^{(2)}_{e,\Lambda\text{-in}/\Lambda'\text{-out}}(t)\right|^2 \tag{8}$$

Using a circularly polarized pump pulse that is incident parallel to the surface normal results in a perturbed ground state orientational distribution $\rho_g(\theta, t = 0)$ at $t = 0$. It is given by $\rho_g(\theta, t < 0)[1 - \eta|\mu|^2|E_c|^2\cos^2(90° - \theta)] = \rho_g(\theta, t < 0)$

$(1-\eta|\mu|^2|E_c|^2\sin^2\theta)$, where 90° − θ is the angle between the circularly polarized light field and the transition dipole for the ground and excited state and η is a collection of constants associated with photoexcitation. The probability of the orientational distribution for the excited state can be expressed as $\rho_g(\theta, t<0)\eta|\mu|^2|E_c|^2\sin^2\theta$. The reasons for using a circularly polarized pump pulse and normal incidence will be discussed later.

For the perturbed ground state, we can write susceptibilities as the following[40]

$$\begin{aligned}\chi^{(2)}_{g,ZZZ}(t=0) &= \alpha^{(2)}_{g,zzz}\int d\theta\,\sin\theta\cos^3\theta[N_g(t<0)\\ &\quad - N_e(\theta,t=0)]\rho_g(\theta,t<0)\\ &= \alpha^{(2)}_{g,zzz}\int d\theta\,\sin\theta\cos^3\theta\, N_g(t<0)\\ &\quad (1-\eta|\mu|^2|E|^2\sin^2\theta)\rho_g(\theta,t<0)\\ \chi^{(2)}_{g,XZX}(t=0) &= \frac{1}{2}\alpha^{(2)}_{g,zzz}\int d\theta\,\sin\theta(\cos\theta-\cos^3\theta)\\ &\quad N_g(t<0)(1-\eta|\mu|^2|E|^2\sin^2\theta)\rho_g(\theta,t<0)\end{aligned} \tag{9}$$

For the excited state, the susceptibilities are

$$\begin{aligned}\chi^{(2)}_{e,ZZZ}(t=0) &= \alpha^{(2)}_{e,zzz}e^{i\delta}\int d\theta\,\sin\theta\cos^3\theta\\ &\quad N_e(\theta,t=0)\rho_g(\theta,t<0)\\ &= \alpha^{(2)}_{e,zzz}e^{i\delta}\int d\theta\,\sin\theta\cos^3\theta\\ &\quad N_g(t<0)\eta|\mu|^2|E|^2\sin^2\theta\,\rho_g(\theta,t<0)\\ \chi^{(2)}_{e,XZX}(t=0) &= \frac{1}{2}\alpha^{(2)}_{e,zzz}e^{i\delta}\int d\theta\,\sin\theta(\cos\theta-\cos^3\theta)\\ &\quad N_e(\theta,t=0)\rho_g(\theta,t<0)\\ &= \frac{1}{2}\alpha^{(2)}_{e,zzz}e^{i\delta}\int d\theta\,\sin\theta(\cos\theta-\cos^3\theta)\\ &\quad N_g(t<0)\eta|\mu|^2|E|^2\sin^2\theta\,\rho_g(\theta,t<0)\end{aligned} \tag{10}$$

where δ is the phase difference between the ground state hyperpolarizability and the excited state hyperpolarizability. In the case of a two-level system, the phase δ is π.[40,41] In our case, the electronic transition of coumarin 314 from S_0 to S_1 is dominant, and coumarin 314 can be approximately considered as a two-level system. Thus, the excited state and ground state of coumarin 314 have hyperpolarizabilities of the same magnitude but opposite signs, that is, $\alpha^{(2)}_{e,zzz} = -\alpha^{(2)}_{g,zzz}$.

As an example, the susceptibilities for P-in/P-out polarization combination the ground state and excited state at $t = 0$ are

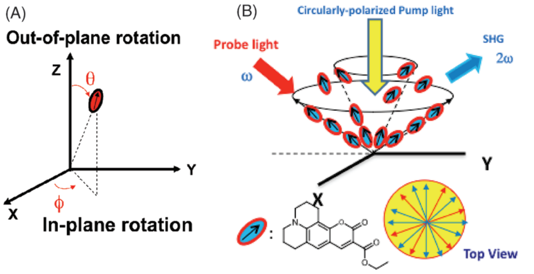

Figure 1. (A) Out-of-plane orientation (θ) and in-plane orientation (ϕ). (B) Schematic of the orientational distribution after photoexcitation. Top view: ground state (blue arrow) and excited state (red arrow) of coumarin 314.

$$\begin{aligned}\chi^{(2)}_{g,\text{P-in/P-out}}(t=0) &= \alpha^{(2)}_{g,zzz}\int A\, d\theta\,\sin\theta(\cos\theta-c\cos^3\theta)\\ &\quad N_g(t<0)(1-\eta|\mu|^2|E|^2\sin^2\theta)\rho_g(\theta,t<0)\\ &= AN_g(t<0)\alpha^{(2)}_{g,zzz}\langle\cos\theta-c\cos^3\theta\rangle_{\rho_g(\theta,t<0)}\\ &\quad - AN_g(t<0)\eta|\mu|^2|E|^2\alpha^{(2)}_{g,zzz}\langle(\cos\theta-c\cos^3\theta)\sin^2\theta\rangle_{\rho_g(\theta,t<0)}\\ \chi^{(2)}_{e,\text{P-in/P-out}}(t=0) &= \alpha^{(2)}_{e,zzz}e^{i\pi}\int A\, d\theta\,\sin\theta(\cos\theta-c\cos^3\theta)\\ &\quad N_g(t<0)\eta|\mu|^2|E|^2\sin^2\theta\,\rho_g(\theta,t<0)\\ &= -\alpha^{(2)}_{g,zzz}AN_g(t<0)\eta|\mu|^2|E|^2\langle(\cos\theta-c\cos^3\theta)\sin^2\theta\rangle_{\rho_g(\theta,t<0)}\end{aligned} \tag{11}$$

By substituting eq 11 into eq 8 for P-in/P-out polarization combination, we obtain, at $t = 0$

$$\begin{aligned}I^{\text{P-in/P-out}}_{\text{total},2\omega}(t=0) &\propto \left|\chi^{(2)}_{g,\text{P-in/P-out}}(t=0)+\chi^{(2)}_{e,\text{P-in/P-out}}(t=0)\right|^2\\ &= \Big|AN_g(t<0)\alpha^{(2)}_{g,zzz}\langle\cos\theta-c\cos^3\theta\rangle_{\rho_g(\theta,t<0)}\\ &\quad - AN_g(t<0)\eta|\mu|^2|E|^2(\alpha^{(2)}_{g,zzz}-\alpha^{(2)}_{e,zzz})\langle(\cos\theta\\ &\quad - c\cos^3\theta)\sin^2\theta\rangle_{\rho_g(\theta,t<0)}\Big|^2\\ &\approx I_{2\omega}(t<0) - 4A^2N_g^2(t<0)\eta|\mu|^2|E|^2(\alpha^{(2)}_{g,zzz})^2\langle\cos\theta\\ &\quad - c\cos^3\theta\rangle_{\rho_g(\theta,t<0)}\langle(\cos\theta-c\cos^3\theta)\sin^2\theta\rangle_{\rho_g(\theta,t<0)}\end{aligned} \tag{12}$$

Thus, a change in SHG intensity from $t < 0$ to $t = 0$ is

$$\begin{aligned}\Delta I^{\text{P-in/P-out}}_{2\omega}(t=0) &= I^{\text{P-in/P-out}}_{2\omega}(t=0)\\ - I^{\text{P-in/P-out}}_{2\omega}(t<0) &= -4A^2N_g^2(t<0)\eta|\mu|^2|E|^2(\alpha^{(2)}_{g,zzz})^2\langle\cos\theta\\ &\quad - c\cos^3\theta\rangle_{\rho_g(\theta,t<0)}\langle(\cos\theta-c\cos^3\theta)\sin^2\theta\rangle_{\rho_g(\theta,t<0)}\end{aligned} \tag{13}$$

Furthermore, we can write the relative change as follows

$$\begin{aligned}\frac{\Delta I_{2\omega}^{\text{P-in/P-out}}(t=0)}{I_{2\omega}^{\text{P-in/P-out}}(t<0)} &= \frac{-4\eta|\mu|^2|E|^2(\langle(\cos\theta - c\cos^3\theta)\sin^2\theta\rangle_{\rho_g(\theta,t<0)})}{(\langle\cos\theta\rangle_{\rho_g(\theta,t<0)} - c\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)})} \\ &= -4\eta|\mu|^2|E|^2\left(1 - \frac{\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)} - c\langle\cos^5\theta\rangle_{\rho_g(\theta,t<0)}}{\langle\cos\theta\rangle_{\rho_g(\theta,t<0)} - c\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)}}\right) \\ &= -4\eta|\mu|^2|E|^2\left(1 - \frac{1 - c\dfrac{\langle\cos^5\theta\rangle_{\rho_g(\theta,t<0)}}{\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)}}}{\dfrac{\langle\cos\theta\rangle_{\rho_g(\theta,t<0)}}{\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)}} - c}\right)\end{aligned} \tag{14}$$

In a similar manner, the relative change in SHG intensity for 45°-in/S-out polarization combination at $t = 0$ is expressed as

$$\frac{\Delta I_{2\omega}^{45^\circ\text{-in/S-out}}(t=0)}{I_{2\omega}^{45^\circ\text{-in/in-out}}(t<0)} = -4\eta|\mu|^2|E|^2\left(1 - \frac{1 - \dfrac{\langle\cos^5\theta\rangle_{\rho_g(\theta,t<0)}}{\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)}}}{\dfrac{\langle\cos\theta\rangle_{\rho_g(\theta,t<0)}}{\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)}} - 1}\right) \tag{15}$$

It is to be noted that for a δ-function distribution, the relative changes in SHG intensity for the 45°-in/S-out and P-in/P-out polarization combinations are equal.

At $t = 0$, the order parameter is

$$R(t=0) = \frac{\langle\cos^3\theta\rangle_{\rho_g(\theta,t<0)}}{\langle\cos^5\theta\rangle_{\rho_g(\theta,t<0)}} \tag{16}$$

Thus, the order parameter, $R(t = 0)$, can be obtained from the ratio of the relative change for the 45°-in/S-out to that for the P-in/P-out at $t = 0$ using eqs 14 and 15.

The order parameters $R(t < 0)$ and $R(t = 0)$, being independent experimental observables, allow us to calculate an orientation distribution function with two unknown variables. If the orientational distribution function is Gaussian

$$\rho = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{(\theta-\theta_0)^2}{2\sigma^2}\right) \tag{17}$$

One can readily obtain the mean orientational angle θ_0 and σ, which is related to the full width at half-maximum (fwhm) $2(2\ln 2)^{1/2}\sigma$, from the measurements of $R(t < 0)$ and $R(t = 0)$.

EXPERIMENTAL SECTION

The experimental aspects of measuring time-dependent SHG responses at the air/water interface have been described earlier.[38,40] In the experiment described here, a femtosecond near IR pulse and a femtosecond visible beam were used as a probe and a pump (Figure 1). A mixed regeneratively and multipass amplified Ti:sapphire laser (Quantronix) was used to generate 3.5 mJ energy, 100 fs duration, and 800 nm wavelength pulses of light at 1 kHz. The pump excitation light at 420 nm was obtained using an optical parametric amplifier (OPA, Clark MXR). The 0.5 μJ pump was focused by a 1 m focal length lens and directed to the sample at normal incidence to a 1 mm diameter spot. A polarizer followed by a quarter-wave plate (zero order quartz at 420 nm) were used to control the polarization. The probe was generated by another OPA (Palitra, Quantronix) sent through a half-wave plate and then focused onto the sample by a lens of 300 mm focal length to a 0.4 mm spot diameter. The probe incidence angle was 70° from normal. The polarization of the probe and the setting of the analyzer could be varied to select the desired input and output polarized combinations. A colored long-wave pass glass filter was placed in the probe beam immediately before the sample to block any spurious source of SH. A polarizer was used to analyze the SHG signal of the desired polarization. Finally, a colored short-wave pass glass filter was used to block any remaining fundamental, and the SHG was focused into a 1/4 m monochromator (Jarrell Ash) and detected by a photomultiplier tube (R4220P, Hamamatsu). The signal from the PMT was gated by a boxcar gated integrator and then fed into a lock-in amplifier, which was synchronized with a 500 Hz chopper in the pump beam. The output from the lock-in amplifier was digitized by a computer A/D board (National Instruments), and the SHG was recorded as a function of time delay between the pump and the probe.

The bulk concentration of coumarin 314 of 15 μM was used for all of the experiments. A shallow Teflon beaker was used to contain the C314 solution. This beaker was rotated at 1 rpm with the probe spot 1 cm off axis to minimize any heating or other photoinduced process in the pump/probe region of the surface.

RESULTS AND DISCUSSION

As shown in Figure 1A, the out-of-plane angle θ subtends the molecular z-axis and the Z-axis normal to the surface plane, and the in-plane ϕ subtends the projection of the molecular axis z in the surface plane. The in-plane ϕ angular distribution is isotropic at equilibrium because the in-plane time-averaged intermolecular forces are isotropic. However, the asymmetry in forces normal to the interface, for example, air above and water below the interface, is responsible for the high degree of orientation for the adsorbates out-of-plane angle θ. The in-plane isotropic orientational distributions for ground state and excited state molecules are depicted schematically in Figure 1B (top view). The reason for our choosing a circularly polarized light that is incident along the surface normal was to achieve the result that both the ground state and the excited state molecules be isotropically distributed in the interface plane. It is because the amplitude of the circularly polarized pump light is isotropic in the interface plane that the excited molecules are also isotropically distributed.

The time-dependent polarized SHG intensities, $I_{2\omega}(t)$, of coumarin 314 at the air/water interface for 45°-in/S-out and P-in/P-out, are shown in Figure 2 (A) and (B). To obtain the order parameter $R(t<0)$, the SHG intensities for 45°-in/S-out and P-in/P-out at $t<0$ were measured. At $t < 0$, the SHG intensity of coumarin 314 for the 45°-in/S-out is 1.8 times that for the P-in/P-out. According to eq 6, the order parameter $R(t < 0)$ was found to be 2.6 ± 0.2.

To obtain the order parameter $R(t = 0)$, the relative change in SHG intensity, $\Delta I_{2\omega}(t = 0)/I_{2\omega}(t < 0)$, for the 45°-in/S-out and the P-in/P-out were measured, making sure that the pump intensities were the same. The time-dependent $\Delta I_{2\omega}(t = 0)/I_{2\omega}(t < 0)$ quantities are shown in Figure 2C. From these curves,

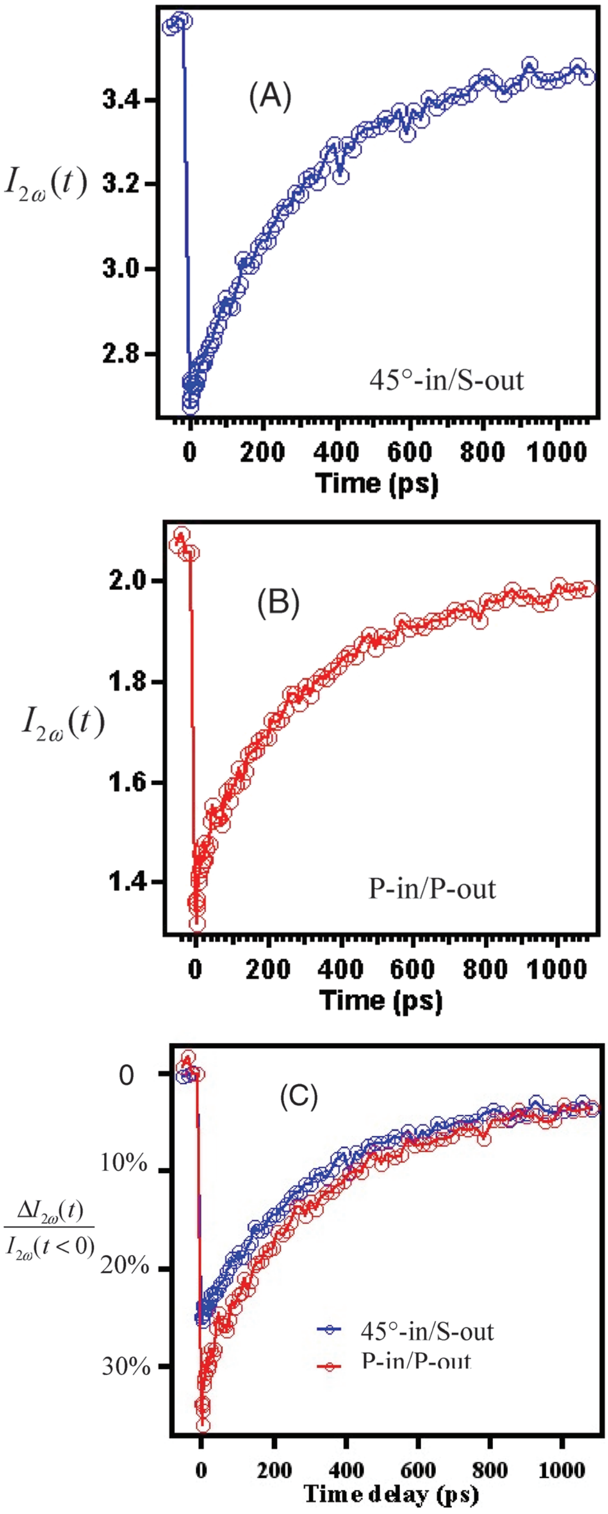

Figure 2. Time-dependent SHG responses for the 45°-in/S-out probe (A) and P-in/P-out (B) polarization combinations. The time dependence of the $\Delta I_{2\omega}/I_{2\omega}(t < 0)$ for both polarization combinations (C).

we obtained the order parameter, $R(t = 0)$ to be 3.1 ± 0.2. With the two independent experimental observables $R(t < 0)$ and $R(t = 0)$, the mean orientational angle and fwhm of a Gaussian distribution were determined to be 55 ± 2° and 16 ± 3°, respectively (Figure 3).

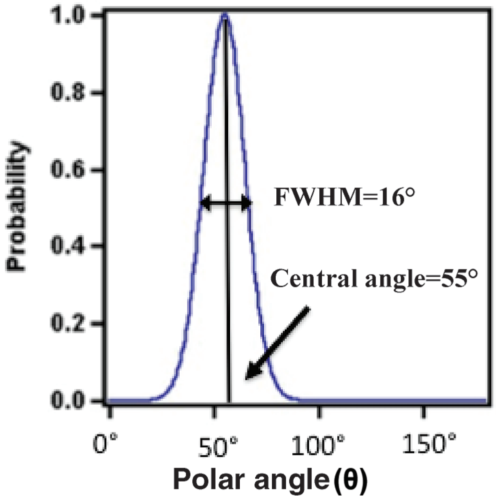

Figure 3. Orientation distribution of ground state coumarin 314 at the air/water interface.

Although we have assumed a particular orientational distribution, namely, Gaussian, our approach can be applied to other distributions having two variables. For example, the wobbling-in-a-cone model has been used to describe orientational diffusion in an environment, for which all of the orientations for a given molecular axis are restricted to be within the cone.[9,30,51] The tilt angle of the cone relative to the surface normal, θ_{LC}, and the half-cone angle θ_S, that is, from one side of the cone to the center of the cone, are combined to depict free diffusion inside the cone.[9,30,51] Within the cone, molecules are assumed to have the same orientational probability. From the two order parameters, $R(t < 0)$ and $R(t = 0)$, the tilt angle θ_{LC} and half-cone angle θ_S were found numerically to be 54 ± 2° and 11 ± 2°, which is very close to those with a Gaussian distribution. It is somewhat surprising that both the Gaussian distribution model and the wobbling-in-a-cone model give similar results.

To summarize, we have presented a direct measurement of orientational distribution width at the air/water interface by using circularly polarized pump and polarized SHG probes. Our approach entailed probing the two different polarization combinations (45°-in/S-out and P-in/P-out), which exhibit distinctive responses to a circularly polarized pump beam along the surface normal. The different responses of the two polarized SHG at $t = 0$ provide an additional order parameter $R(t = 0)$. Taken together with the order parameter $R(t < 0)$ at equilibrium, that is, before the pump pulse, the mean orientational angle, and its distribution width of coumarin 314 molecules at the air/water interface were determined. The experimental result indicates that coumarin 314 dye molecules show a broad orientation distribution of 16° at the air/water interface.

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